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Comparison of Methods for the Determination of Total Available Residual Chlorine in Various Sample Matrices

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The information obtained can be used by the analyst in determining which method is most suitable for a particular matrix. The data show the importance of the nature of the sample matrix. The necessity of comparing several methods in order to be certain of the accuracy is also obvious given the data.

This report covers a period from March 1976 to November 1976 and was completed as of November 12, 1976..

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COMPARISON OF METHODS FOR THE DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN VARIOUS SAMPLE MATRICES

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water; and to determine the responses of aquatic organisms to water quality.

- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

The amendments to the guidelines establishing test procedure for the analysis of pollutants published in the Federal Register, December 1, 1976, specify the methods that are approved for the analysis of total available residual chlorine. Among these methods are the iodometric titration, the amperometric titration, and the iodometric and amperometric back titrations. The N,N-diethyl-p-phenylenediamine (DPD) colorimetric and titrimetric methods have been given interim approval pending laboratory investigation. This report is a laboratory investigation of these methods as well as several recently developed methods and some test kits which employ the DPD colorimetric procedure. The methods are applied, without modification, to various sample matrices. Accuracy relative tc the colorimetric titration method and precision are determined.

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ABSTRACT

Ten different methods for determining total available residual chlorine, all based on the iodine-iodide reaction, were tested without modification on four sample matrices. Their precision was determined by seven replicate determinations. Accuracy, as compared to the iodometric starch titration method, was determined in terms of percent yield. Observations regarding advantages, disadvantages, deviations from the expected and problems involved in the determination are recorded. The data are presented in tables arranged for instructive purposes and in a figure intended to present the data in reduced form for easier appraisal.

The information obtained can be used by the analyst in determining which method is most suitable for a particular matrix. The data show the importance of the nature of the sample matrix. The necessity of comparing several methods in order to be certain of the accuracy is also obvious given the data.

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SECTION I

INTRODUCTION

Total available residual chlorine analysis is important in monitoring the safety of drinking water to insure that the proper level needed to destroy harmful organisms is maintained. It is also important in determining the amount of residual chlorine needed to properly treat sewage and industrial wastewater. The amount of residual chlorine present must be adequate for disinfection, yet not be so much in excess as to cause detriment to the body of water into which it is discharged.

There can be a large variation in the composition of sewage and industrial wastewater insofar as interferences are concerned. The amount of turbidity, organic matter, ionic material, solids, color, buffering capacity and overall clarity can vary greatly. The choice of analytical method depends upon the nature of the sample as well as on the analytical parameters of the available methods themselves. The fact that the analysis must be performed immediately on site due to the ephemeral nature of residual chlorine must also be considered.

The procedures for the determination of total available residual chlorine are actually measures of the total oxidizing power of the solution. There are a number of components of the solution that are responsible for this oxidizing property. When determining one particular oxidizing agent, the others are regarded as interferences that must be eliminated or otherwise accounted for. In a chlorination operation the predominant oxidizing power comes from the chlorination process; other minor constituents contribute negligibly and can be ignored. There are some modifications to the procedure to eliminate interfering oxidizing agents where they are known to be present in concentrations that interfere significantly.

When chlorine or calcium hypochlorite is added to water it becomes hypochlorite ion, referred to as free available chlorine. If ammonia is present, as is usually the case, chloramines form. These chloramines are referred to as combined available chlorine. The total available residual chlorine procedures studied here simultaneously determine free and combined available chlorine.

All of the studied methods involve the same basic reaction: the oxidation of iodide reagent to iodine in a solution buffered af pH 4. The main difference between the methods is in how the iodine is determined. There are also minor differences in the nature of the buffer and reagent concentrations. The result is calculated as mg/l chlorine using the molecular weights of the species involved.

The recommended method for the determination of total available residual chlorine in sewage and industrial wastewater effluents is the iodometric back titration using an amperometric endpoint. Variations such as the forward titration or the use of a starch endpoint are allowed as the nature of the sample permits. The N,N-diethyl-p-phenylenediamine (DPD) colorimetric or titrimetric methods are permitted as interim methods pending laboratory evaluation (1,2).

There are a large number of other available methods which have been compared in the literature (3-6). Some of the comparisons involve the determination of free rather than total available residual chlorine; however, much of the information concerns questions related to both determinations because of the similarities between them. There are some variations in the application of the amperometer and the DPD method due to commercially designed instruments and kits. In addition there are new or newly improved electrochemical methods not compared previously.

This study was initiated to provide information on which a decision can be based as to which method is most appropriate for particular sample matrices. Data were investigated concerning the precision, accuracy, range and other factors as well as the general advantages, disadvantages and problems likely to be encountered in applying the methods to actual samples. The study covers the approved methods, some commercial variations of the approved methods and some new electrochemical methods and instrumentation.

SECTION II

SUMMARY AND CONCLUSION

The following figure is a schematic representation showing the relative accuracy of the methods. The figure is a convenient and instructive means of comparing the various methods and an aid in selecting the proper method. For drinking water only the CN-66 is far out of line. For river water the results are spread over a wide range of relative accuracies with the titrimetric methods grouped together. For the secondary treated sewage the methods can be placed into a number of overlapping groups, making the drawing of conclusions difficult.

Each of the methods has been shown to work well in certain matrices but not in others. This emphasizes the importance of the nature of the sample matrix. Turbidity, color, buffering capacity and ionic content are obvious factors to consider in selecting a method. Comparison of each method with at least one of the methods recommended in the Federal Register should be made to insure that the results are compatible. This is expecially true for industrial wastewaters.

The data in this report will provide information in determining which methods are most likely to be successful for a particular sample matrix. When other than an approved (2) method is desired, the desired mechanism of obtaining alternate test procedure approval for compliance with legislation must be used.

SECTION III

EXPERIMENTAL

REAGENTS AND EQUIPMENT

The reagents and their preparation are described in the references pertaining to the individual methods as mentioned further into this report. Commercially prepackaged reagents were used where available.

Commercially available microburets in the zero to ten and zero to two millimeter range were also used. The spectrophotometer was a single beam, digital readout Perkin-Elmer Coleman 54B. The sample holder, cell and amperometer of a Wallace and Tiernan Amperometric Titrator were used. Due to the age of the various rubber valves of the delivery system, the volume of reagent delivered in each case was in error. It was decided that a microburet would be more precise and was therefore used. The delivery system was replaced by running a piece of tubing from the tip of the microburet to the cell. The tubing was washed with distilled water after each day of use in order to minimize damage due to contact time with the reagents. An Orion Residual Chlorine Selective Ion Electrode and Model 801 Digital Readout Expanded Scale pH Meter were used. A prototype model of the NBS Residual Chlorine Flux Monitor was also evaluated. Because there are so many kit forms of the DPD colormetric method available, only two were chosen as representative of DPD kits: The Hach CN-66 kit and the Bausch and Lomb Mini-20 Portable Spectrophotometer with a kit of reagents.

ANALYTICAL METHODS

The following methods were compared using procedures as described in the references. The nomenclature given below is used in the tables for conciseness.

Iodo-I: This appears in reference (7), page 316, as "Method 409A Iodometric Method I." It is the forward titration with 0.00564 N phenylarsine oxide (PAO). The PAO reagent was purchased from Wallace and Tiernan and checked by titrating with primary standard potassium biiodate solution prepared in the laboratory. The blank correction was found to be negligible with the distilled water and the reagents used.

Iodo-II: This appears in reference (7), page 318, as "Method 409B Iodometric Method II." It is the back titration with 0.0282 N iodine. The iodine released by the reaction of the reagents with the sample is immediately consumed by 0.00564 N phenylarsine oxide. The excess PAO is then titrated with 0.0282 N iodine. (The normality of the iodine was actually slightly less, but a correction factor was used in the calculations so that the number of milli-

liters of iodine was corrected for the nomality.)

Amp-I: This appears in reference (7), page 322, as "Method 409C Amperometric Titration Method" and in the manual (8), supplied with the Wallace and Tiernan Instrument. The prepackaged reagent solutions that come with the Wallace and Tiernan instrument were used, but the delivery system was not (see above). The method is essentially the same as Iodo-I except that the endpoint involves the deflection of the amperometer needle instead of the observation of the starch color change.

Amp-II: This appears in reference (7), page 318, as part of "Method 409B Iodometric Method II" and in the Wallace and Tiernan manual. It is essentially the Iodo-II method with an amperometric endpoint instead of a starch endpoint.

DPD-FAS: This appears in reference (7), page 329, as "Method 409E DPD Ferrous Titrimetric Method." Only the total available residual chlorine determination was performed, thus iodine was being titrated by standard ferrous ammonium sulfate solution in all cases.

DPD Colorimetric: This appears in reference (7), page 322, as "Method 409F DPD Colorimetric Method." The 12 X 75 cm mini curvettes were used in the Perkin Elmer Coleman 54B Spectrophotometer. The procedure for total available residual chlorine (by going straight to step 4e) was used. After the absorbances of the standard solutions were determined, they were titrated with FAS. This experimentally obtained number was then used to calculate the calibration curve.

Flux Monitor: The National Bureau of Standards has developed an instrument that electrochemically measures iodine flowing through a cell (9,10). A number of prototype models are being tested in various laboratories. One of these prototypes was made available to EMSL - Cincinnati for testing. The investigation in this laboratory was concerned with performance and applicability to various matrices. The electronic circuitry and mechanical flow operation was not studied; however, some information concerning these characteristics was obtained as problems arose and is included in the discussion.

Electrode: Selective-ion electrodes are available for the measurement of total available residual chlorine. The principle involves the oxidation of iodide in the presence of pH 4 buffer. Instead of a titration or a colorimetric reading, the iodine is measured by an electrode. The Orion electrode and system were arbitrarily selected for this study. The procedure used was that provided in the Orion manual (11).

CN-66: A large number of kits are available that utilize the DPD Colorimetric method. The Hach CN-66 kit was chosen as being representative. The directions and prepackaged reagents that accompany the kit were used (12).

Mini-20: The Bausch and Lomb total available residual chlorine kit, utilizing a portable spectrophotometer called the Mini-20, was arbitrarily selected as another kit form of the DPD colorimetric method. The direction and prepackaged reagents supplied with the kit were used (13).

SAMPLES AND SAMPLE PREPARATION

Samples chosen for study included distilled water, tap water, river water, a sewage plant effluent and raw sewage. All but the tap water required the addition of chlorine in the form of calcium hypochlorite.

This was prepared as a saturated calcium hypochlorite solution and stored in a dark bottle. This was added to each sample matrix when needed in order to produce the desired concentration of hypochlorous ions. The exact concentration was then determined by the Iodo-I method. This method served as the standard of comparision throughout; all comparisions were made relative to the Iodo-I result as the arbitrarily chosen true value.

The sample matrix water was placed in a 3-liter volumetric flask equipped with a ground glass stopper. If necessary some saturated calcium hypochlorite was added to adjust the level of chlorine. As a rule of thumb four drops would produce 0.5-1.0 mg/l concentration, however if a demand was present, adjustment became more difficult. Samples of river water and sewage were under constant aeration to retard the production of anaerobic bacteria.

The chlorine was adjusted by determining the concentration by the Iodo-1 method. Seven replicates were immediately run by the method being compared. Then another run was made by the Iodo-I method. The values of the two Iodo-I determinations were often exactly the same or were extremely close so that their average could be called the "true value."

Distilled Water: The distilled water was passed through a Millipore Super-Q system and was found to be chlorine and chlorine-demand free.

Drinking Water: This was taken from the coldwater tap in the laboratory. No spike was necessary.

River Water: Five gallons of sample was collected from the Ohio River, brought to the laboratory and put under aeration. The seven replicates for the ten procedures were run as rapidly as possible, requiring approximately a week.

Chlorine had to be added to satisfy the demand and produce a useful concentration. There was no naturally occuring chlorine level.

Secondary Treated Sewage: A 5-gallon sample of secondary treated sewage was taken at the Clermont County Sewage Treatment Works. The source of the sewage was primarily of commmunity origin. There was a "natural" chlorine level (i.e., added during treatment) that gradually dissipated over several days, so that eventually some saturated calcium hypochlorite solution had to be added to the volumetric flask. The sample was clear to very slightly yellow.

Raw Sewage: Five gallons of sample were collected at the Cincinnati Sewage Treatment Plant. The source was of mixed domestic and industrial origin and had received no treatment. The sample was deep straw colored with high solids content. These varied from fine, non-settlement to large, settleable

particles. The 5-gallon carboy was swirled before transfer to the 3-liter flask to maintain the most difficult possible sample as a stringent test of those methods that could be applied to this sample.

SECTION IV

RESULTS AND DISCUSSION

Three replicates of calcium hypochlorite in distilled water were run in order to eliminate from consideration any method that may be totally imprecise as well as to obtain a feeling for what to expect in analyzing more complex samples. The results are shown in Tables 1 through 10. Various levels were determined except for the Flux monitor and the Mini-20 whose ranges are more limited. As all methods were found to be precise, accuracy data in the distilled water matrix were not determined having little practical value. However, accuracy data were obtained for the two DPD kits using a distilled water matrix because kits are often inaccurate, having sacrificed accuracy for simplicity. The individual methods are discussed below.

METHODS

Iodo-I The Iodo-I method was found to be applicable to all of the sample matrices studied, although the end point was difficult to observe for the raw sewage. The fact that most methods were within 10% of the value obtained by the Iodo-I method made its choice as the arbitrary true value credible. Had there been large differences in results, the Amp-II method would have been used for this purpose. Results indicating the precision of the method are shown in Table 1. As expected, the precision is better for simple matrices and at higher concentrations. The difficulty in perceiving the end point is largely responsible for any poorer precision obtained, especially in the case of raw sewage samples. Another factor of interest, not pursued here, is the delay in the formation of the blue color in the raw sewage samples. This phenomenom might be peculiar to this sample and was not investigated because raw sewage samples are seldom analyzed for this constituent. They were used here merely to test the method under extreme conditions.

Iodo-II The titration of excess PAO with iodine using a starch end point produced results (Table 2) that lead to the conclusion that the method is equivalent to the Iodo-I procedure for these particular samples. The maximum possible volume of titrant is 1 ml, otherwise the concentration of total available residual chlorine is calculated to be a negative number. This leads to less precision because of more potential experimental error.

Amp-I The titration of iodine with PAO using an amperometric end point is reasonably precise and accurate for certain samples. The results (Table 3) are low for sewage samples as described, especially for raw sewage where the recovery is actually 44%. The suggestion (8) that Amp-II be used instead is verified, although the fact that the Iodo-I method works and has the same initial chemistry leads to the conclusion that perhaps some research with varying reagent concentrations might produce a more useful method.

TABLE 1. PRECISION FOR THE DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN VARIOUS SAMPLE MATRICES BY THE IODO-I METHOD

SAMPLE[a] MATRIX	AVERAGE mg/l	STANDARD DEVIATION ± mg/l	RELATIVE STANDARD DEVIATION, %
Distilled Water	0.25	0.001	0.23
	4.02	0.03	0.76
Drinking Water	0.68	0.04	5.2
River Water	0.30	0.03	9.7
Domestic Sewage	1.11	0.06	5.9
Raw Sewage	0.48	0.09	18.0

[a] Three replicates for distilled water. Seven replicates for other samples.

TABLE 2. PRECISION AND ACCURACY FOR THE DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN VARIOUS SAMPLE MATRICES BY THE IODO-II METHOD

SAMPLE MATRIX [a]	AVERAGE mg/l	STANDARD DEVIATION ± mg/l	RELATIVE STANDARD DEVIATION, %	TRUE VALUE [b]	%RECOVERY
Distilled Water	0.41	0.05	12.2	----	----
	3.51	0.12	3.3	----	----
Drinking Water	0.84	0.04	4.3	0.85	98.8
River Water	0.84	0.02	2.7	0.78	107.7
Domestic Sewage	0.87	0.07	7.6	1.00	87.0
Raw Sewage	0.55	0.09	16.0	0.5[c]	100[c]

[a] Three replicates for distilled water. Seven replicates for other samples.

[b] Arbitrarily assigned to the Iodo-I value.

[c] This sample at the time run was fading rapidly. This is reflected in the high standard deviation as well as in the attempt to accurately determine the true value at any given time.

TABLE 3. PRECISION AND ACCURACY OF THE DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN VARIOUS SAMPLE MATRICES BY THE AMP-I METHOD

SAMPLE[a] MATRIX	AVERAGE mg/l	STANDARD DEVIATION ± mg/l	RELATIVE STANDARD DEVIATION, %	TRUE[b] VALUE	%RECOVERY
Distilled Water	0.38	0.02	6.1	----	----
	3.50	0.006	0.16	----	----
Drinking Water	0.97	0.03	2.6	0.94	103.2
River Water	0.57	0.02	3.0	0.56	101.8
Domestic Sewage	0.41	0.03	6.9	0.50	82.0
Raw Sewage[c]	----	----	----	----	----

a Three replicates for distilled water. Seven replicates for other samples.

b Arbitrarily assigned to the Iodo-I value.

c Very poor recovery, see text.

Amp-II The titration of excess PAO with iodine using an amperometric endpoint produces the results shown in Table 4. The method worked well in drinking water and distilled water, however the accuracy was low for secondary-treated sewage. The results for raw sewage could not be determined. For raw sewage sample wherein 0.21 mg/l was obtained by the Amp-II method, the DPD-FAS Method gave 0.11 mg/l and the Iodo-II Method, 1.01 mg/l. The sample was too complex to allow comparison.

DPD-FAS Results of the titration of iodine produced from potassium iodide with ferrous ammonium sulfate using DPD as the indicator agree with results of the Iodo-I Method to a remarkable degree even in spiked raw sewage (Table 5). The actual reading was consistently somewhat higher by 6 to 8%, within one standard deviation. For the raw sewage the endpoint is difficult to observe but not as difficult as that for starch. Of course, neither result is necessarily correct for raw sewage, based on the results obtained in the Amp-II experiments above. On another raw sewage sample the DPD-FAS gave a value of 0.80 mg/l whereas the Amp-I gave a result approximately 50% lower (0.35 mg/l).

The color intensifies with the first addition of FAS, and increases with each additional increment, followed by some fading. The mechanism of this phenomenon is not understood, but could be useful in increasing the sensitivity of the DPD-Colorimetric Method. The value obtained by this method was consistently 6 to 8% higher than that obtained by the Iodo-I method. Although the values are within one standard deviation of one another, and thus considered the same member, the bias was always positive.

DPD Colorimetric The DPD colorimetric method also consistently produces a slightly higher result than the Iodo-I Method (Table 6). In addition, the presence of color and solids in the sample presents a problem; thus, the raw sewage could not be run by this method.

The calibration curve does not follow Beer's Law; it is slightly curved. Also, there is some fading that increases as the concentrations increase. This may be the reason for the calibration curve being non-linear.

Flux Monitoring The Flux Monitor gave fairly precise and accurate results for river water (Tabel 7). Solid material must be absent because of the narrow passages of the cell and the flowmeter. Passage of the sample through a filter has been suggested as a correction for this; however, the filter also gradually clogs and affects the flow. The flow is extremely sensitive to the head pressure from both the sample intake and drain tubes. The height of each in relation to the console of the instrument is critical in determining whether the rheostatically controlled pump can achieve the flow rate necessary for the digital readout to be directly in mg/l. As both the intake and drain must be below the instrument, it was placed 18 in. above the bench surface on which the sample container and drain were placed.

The flowmeter reading often drifted, thus requiring close attention. Control of the line voltage (which causes variations in the pump speed) or a different flowmeter might improve the flow characteristics of the system. Flowmeters that contain metal valves have proven susceptible to corrosion by iodine (14).

TABLE 4. PRECISION AND ACCURACY OF THE DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN VARIOUS SAMPLE MATRICES BY THE AMP II METHOD

SAMPLE[a] MATRIX	AVERAGE mg/l	STANDARD DEVIATION ± mg/l	RELATIVE STANDARD DEVAITION, %	TRUE[b] VALUE	%RECOVERY
Distilled Water	0.58	0.05	8.8	----	----
	3.53	0.07	2.0	----	----
Drinking Water	0.82	0.05	5.9	0.83	98.8
River Water	0.68	0.06	9.4	0.66	103.0
Domestic Sewage	1.10	0.09	8.3	1.45	75.7
Raw Sewage[c]	0.21	0.09	41.0	----	----

a Three replicates for distilled water. Seven replicates for other samples.

b Arbitrarily assigned to the Iodo-I value.

c This sample gave 0.11 by the DPD-FAS METHOD and 1.01 by the Iodo-II Method.

TABLE 5. PRECISION AND ACCURACY OF THE DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN VARIOUS SAMPLE MATRICES BY THE DPD-FAS METHOD

SAMPLE[a] MATRIX	AVERAGE mg/l	STANDARD DEVIATION ± mg/l	RELATIVE STANDARD DEVIATION, %	TRUE[b] VALUE	%RECOVERY
Distilled Water	0.34	0.02	5.6	----	----
	0.65	0.003	0.5	----	----
	3.45	0.02	0.5	----	----
Drinking Water	0.98	0.01	1.2	0.91	107.7
River Water	0.79	0.01	1.4	0.73	108.2
Domestic Sewage	1.08	0.02	1.8	1.20	90.0
Raw Sewage	0.79	0.03	3.3	0.75	105.3

a Three replicates for distilled water. Seven replicates for other samples.

b Arbitrarily assigned to the Iodo-I value.

TABLE 6. PRECISION AND ACCURACY OF THE DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN VARIOUS SAMPLE MATRICES BY THE DPD COLORIMETRIC METHOD

SAMPLE MATRIX	AVERAGE mg/l	STANDARD DEVIATION + mg/l	RELATIVE STANDARD DEVIATION, %	TRUE[b] VALUE	%RECOVERY
Distilled Water	0.39	0.012	3.1	----	----
	3.61	0.11	3.2	----	----
Drinking Water	0.94	0.008	0.8	0.86	109.3
River Water	0.86	0.02	1.9	0.70	122.9
Domestic Sewage	1.07	0.03	2.4	1.01	106.0
Raw Sewage[c]	----	----	----	----	----

a Three replicates for distilled water. Seven replicates for other samples.

b Arbitrarily assigned to the Iodo-I value.

c Too much color and solids to be run.

TABLE 7. PRECISION AND ACCURACY OF THE DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN VARIOUS SAMPLE MATRICES BY THE FLUX MONITOR

SAMPLE[a] MATRIX	AVERAGE mg/l	STANDARD DEVIATION ± mg/l	RELATIVE STANDARD DEVIATION, %	TRUE[b] VALUE	%RECOVERY
Distilled Water	0.54	0.04	7.5	----	----
Drinking Water	0.84	0.02	1.9	0.91	92.3
River Water	0.39	0.07	17.1	0.50	78.0
Domestic Sewage	0.74	0.02	2.6	0.75	98.7
Raw Sewage[c]	----	----	----	----	----

a Three replicates for distilled water. Seven replicates for other samples.

b Arbitrarily assigned to the Iodo-I value.

c Too high in solids to risk running. Previous researchers experienced clogging in the cell.

There is a great deal of noise within the digital readout, especially when setting the high standard value at 0.433 mg/l. It has been suggested (14) that this may be due to improper mixing as the stream flows from the standard generating cell to the detector cell and that some adjustment could be made to correct for this in future design generations of the instrument.

In the batch operation using distilled water, the response time--from zero to the sample reading--was approximately 3 minutes, during which approximately 400 ml of sample were consumed. However, once continuous monitoring has begun and the instrument is no longer starting at zero millivolts, the response time may be faster.

During analysis of tapwater, bubbles formed and could be observed on the flowmeter walls. They form on the flowmeter ball and effect the flow reading as well as forming in the detector cell where they effect the millivolt output reading. They must be mechanically removed by tapping. The bubble formation has been attributed to supersaturation when the water was put under pressure for delivery (14).

Electrode The electrode was found to be accurate for drinking water and one particular sample of secondary-treated sewage. However, river water and a different sample of the same source of secondary sewage had low results. Raw sewage tests produced a continuous upward drift (Table 8). The pH of the secondary treated sewage was initially 8.7; after the reagents were added it was 4.1, and therefore the capacity was not exceeded. The iodate standard was titrated and was found to be correct.

CN-66 This kit produced unacceptably high results for drinking water, extremely low results for river water but only slightly high results in distilled water and secondary treated domestic sewage. The precision was remarkable considering the subjective nature of the colorimetric measurement (Table 9).

When the concentration of total available residual chlorine is above the maximum concentration shown on the color wheel (e.g. approximately 5 mg/l) the color is a slightly different shade. This could be useful as a warning signal. If this slightly-off shade is matched it will give a false reading. For example the slightly-off shade read 2.68 mg/l on the color wheel when it read 5.32 mg/l by the DPD Colorimetric Method.

It has been reported (15) that the color wheel fades in the presence of sunlight. This was not investigated in this work, but it is a possible difficulty that must be considered if outdoor readings are involved and should be checked occasionally even if it is only used in indoor lighting situations.

Mini-20 The comparison of results (Table 10) shows that the method produces precise but inaccurate results. Results were very much higher for distilled water and drinking water, somewhat lower for secondary treated domestic sewage and very much lower for river water.

COMPARISON

In order to more conveniently compare the methods for a particular sample

TABLE 8. PRECISION AND ACCURACY OF THE DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN VARIOUS SAMPLE MATRICES BY THE ELECTRODE

SAMPLE[a] MATRIX	AVERAGE mg/l	STANDARD DEVIATION ± mg/l	RELATIVE STANDARD DEVIATION ,%	TRUE[b] VALUE	%RECOVERY
Distilled Water	0.34	0.003	0.9	----	----
	3.85	0.07	1.7	----	----
Drinking Water	0.88	0.03	3.1	0.84	104.8
River Water	0.72	0.02	3.3	0.96	75.0
Domestic Sewage	0.71	0.03	3.8	0.95	75.0
	0.83	0.04	4.7	0.80	103.8
Raw Sewage[c]	----	----	----	----	----

a Three replicates for distilled water. Seven replicates for other samples.

b Arbitrarily assigned to the Iodo-I value.

c Millivolt reading continuously increased. Sample gave 2.5 ± 0.2 mg/l by electrode, 3.6 mg/l by Amp II and 8.5 mg/l by DPD-FAS at this time.

TABLE 9. PRECISION AND ACCURACY OF THE DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN VARIOUS SAMPLE MATRICES BY THE CN-66 KIT

SAMPLE[a] MATRIX	AVERAGE mg/l	STANDARD DEVIATION ± mg/l	RELATIVE STANDARD DEVIATION,%	TRUE VALUE[b]	%RECOVERY
Distilled Water[c]	0.44	0.012	2.6	----	----
	1.43	0.006	0.4	----	----
Drinking Water	1.22	0.04	3.4	0.91	134.1
River Water	0.39	0.02	4.2	0.75	52.0
Domestic Sewage	1.92	0.10	5.1	1.75	109.7
Raw Sewage[d]	----	----	---	----	----

a Three replicates for distilled water. Seven replicates for other samples.

b Arbitrarily assigned to the Iodo-I value.

c When the same solutions were transferred to a spectrophotometer cell and read, then compared to a standard curve prepared as in the DPD Colorimetric Method the results were 0.42 ± 0.02 mg/l and 1.35 ± 0.03 mg/l. If these values are called the "true value" the recoveries from the kit method are 105% and 106% respectively.

d Turbidity and deep straw color prevented raw sewage from being analyzed.

TABLE 10. PRECISION AND ACCURACY OF THE DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN VARIOUS SAMPLE MATRICES BY THE MINI-20 METHOD

SAMPLE[a] MATRIX	AVERAGE mg/l	STANDARD DEVIATION ± mg/l	RELATIVE STANDARD DEVIATION, %	TRUE[b] VALUE	%RECOVERY
Distilled Water	0.44	0.01	2.3	0.30	146.7
Drinking Water	0.45	0.02	3.9	0.40	112.5
River Water	0.16	0.01	6.0	0.65	24.6
Domestic Sewage	0.58	0.03	5.0	0.75	77.0
Raw Sewage					

a Three replicates for distilled water Seven replicates for other samples.

b Arbitarily assigned to the Iodo-I value.

matrix the data from the first ten tables have been rearranged into Tables 11 through 14. From these data the following conclusions have been established.

Distilled Water All of the methods are accurate to less than 12.2%, the deviation being greater at lower concentrations. This is single laboratory, single operator precision based on only three determinations. The purpose was to clearly identify inferior methods, of which there are none (Table 11).

Drinking Water Seven replicates were run. The precision was calculated and the average compared with the results obtained by the Iodo-I Method as an arbitrary measure of the accuracy. All of the results (Table 12) were within 10% except for the Mini-20 (12.5% high) and then the CN-66 (34.1% high).

River Water The titration methods, forward and back, were slightly high compared with the Iodo-I Method, but were within 10%. The DPD Colorimetric Method was very high (22.9%). The electrical methods were low and the kits were very low (Table 13). For the kits, a study involving pH and the amounts and concentrations of the reagents is indicated because the laboratory DPD Colorimetric Method produced results with the error in the opposite direction.

Secondary Treated Sewage With this sample the methods produced several groups of values (Table 14). The DPD-FAS, DPD Colorimetric Flux Monitor and CN-66 were within 10% of the Iodo-I Method. The Iodo-II, Amp I, Amp II, Electrode and Mini-20 were lower, but were grouped within slightly greater than 10% error of one another. In view of the arbitrary nature of the choice of Iodo-I as the standard of comparison, it is difficult to state that one set is low or the other set high.

Raw Sewage Raw mixed domestic and industrial sewage was used as a matrix in order to provide an extremely complex sample. It contained a high chlorine demand that had to be satisfied before the level in the range of the methods could be attained. Extremely erratic results were obtained when it was run by different methods (Table 15). Fresh sample remained constant enough for the analysis of seven replicates, but as the sample aged the chlorine value began fading rapidly over the seven replicate determinations (Table 15, run number 4).

The starch endpoint could be observed but with difficulty. The DPD-FAS endpoint was slightly easier to observe. For the electrode the millivolt reading continually drifted upward. Because of the color and/or solids, a number of methods could not be run with this sample.

The amperometric endpoint produced no problem in observation. However, the accuracy of the results for the Amp II, while difficult to assess, appears to be poor.

TABLE 11. PRECISION OF TOTAL AVAILABLE RESIDUAL CHLORINE DETERMINATION OF CALCIUM HYPOCHLORITE IN DISTILLED WATER

METHOD	AVERAGE[a] mg/l	STANDARD DEVIATION ± mg/l	RELATIVE STANDARD DEVIATION, %
Iodo-I	0.25	0.001	0.23
	4.02	0.03	0.76
Iodo-II	0.41	0.05	12.2
	3.51	0.12	3.3
Amp-I	0.38	0.02	6.1
	3.50	0.006	0.16
Amp-II	0.58	0.05	8.8
	3.53	0.07	2.0
DPD-FAS	0.34	0.02	5.6
	0.65	0.003	0.5
	3.45	0.02	0.5
DPD Color	0.39	0.012	3.1
	3.61	0.11	3.2
Flux Monitor	0.54	0.04	7.5
Electrode	0.34	0.003	0.9
	3.85	0.07	1.7
CN-66	0.44	0.012	2.6
	1.43	0.006	0.4
Mini-20	0.44	0.01	2.3

a Three determinations.

TABLE 12. DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN DRINKING WATER

METHOD	AVERAGE mg/l	STANDARD DEVIATION ± mg/l	RELATIVE STANDARD DEVIATION, %	TRUE VALUE[b]	%RECOVERY
Iodo-I	0.68	0.04	5.2	----	----
Iodo-II	0.84	0.04	4.3	0.85	98.8
Amp-I	0.97	0.03	2.6	0.94	103.2
Amp-II	0.82	0.05	5.9	0.83	98.8
DPD-FAS	0.98	0.01	1.2	0.91	107.7
DPD Color	0.94	0.008	0.8	0.86	109.3
Flux Monitor	0.84	0.02	1.9	0.91	92.8
Electrode	0.88	0.03	3.1	0.84	104.8
CN-66	1.22	0.04	3.4	0.91	134.1
Mini-20	0.45	0.02	3.9	0.40	112.5

a Seven replicates

b Arbitrarily assigned to Iodo-I value

TABLE 13. DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN RIVER WATER

METHOD	AVERAGE mg/l	STANDARD DEVIATION ± mg/l	RELATIVE STANDARD DEVIATION, %	TRUE[b] VALUE	%RECOVERY
Iodo-I	0.30	0.03	9,7	----	----
Iodo-II	0.84	0.02	2.7	0.78	107.7
Amp-I	0.57	0.02	3.0	0.56	101.8
Amp-II	0.68	0.06	9.4	0.66	103.0
DPD-FAS	0.79	0.01	1.4	0.73	108.2
DPD Color	0.86	0.02	1.9	0.70	122.9
Flux Monitor	0.39	0.07	17.1	0.50	78.0
Electrode	0.72	0.02	3.3	0.96	75.0
CN-66	0.39	0.02	4.2	0.75	52.0
Mini-20	0.16	0.01	6.0	0.65	24.6

a Seven replicates

b Arbitrarily assigned to Iodo-I value.

TABLE 14. DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN SEWAGE AFTER SECONDARY TREATMENT

METHOD	AVERAGE[a] mg/l	STANDARD DEVIATION ± mg/l	RELATIVE STANDARD DEVIATION, %	TRUE[b] VALUE	%RECOVERY
Iodo-I	1.11	0.06	5.9	----	----
Iodo-II	0.87	0.07	7.6	1.00	87.0
Amp-I	0.41	0.03	6.9	0.50	82.0
Amp-II	1.10	0.09	8.3	1.45	75.9
DPD-FAS	1.08	0.02	1.8	1.20	90.0
DPD Color	1.07	0.03	2.4	1.01	106.0
Flux Monitor	0.74	0.02	2.6	0.75	98.7
Electrode	0.71	0.03	3.8	0.95	75
	0.83	0.04	4.7	0.80	103.8
CN-66	1.92	0.10	5.1	1.75	109.7
Mini-20	0.58	0.03	5.0	0.75	77.0

a Seven replicates

b arbitrarily assigned to Iodo-I value.

TABLE 15. DETERMINATION OF TOTAL AVAILABLE RESIDUAL CHLORINE IN RAW SEWAGE CHLORINATED IN LABORATORY

RUN NUMBER	METHOD	mg/l
1.	Amp-II	0.21
	DPD-FAS	0.11
	Iodo-II	1.01
2.	Iodo-I	0.75
	DPD-FAS	0.79 ± 0.03
3.	Amp-I	0.35
	DPD-FAS	0.80
4.	Iodo-II	0.55 ± 0.09
	DPD-FAS	0.76 initial-
		0.40 final
5.	Amp-II	3.55
	DPD-FAS	8.45
	Electrode	continuous drift, two determinations (A and B)

	A	B
After 5 minutes	2.25	2.17
After 15 minutes	2.73	2.73

NOTE: in run number 1- Iodo-II >>DPD-FAS, in run number 4 Iodo≈ DPD-FAS and in run number 1, DPD-FAS <Amp-II while in run number 5 DPD-FAS> Amp-II.

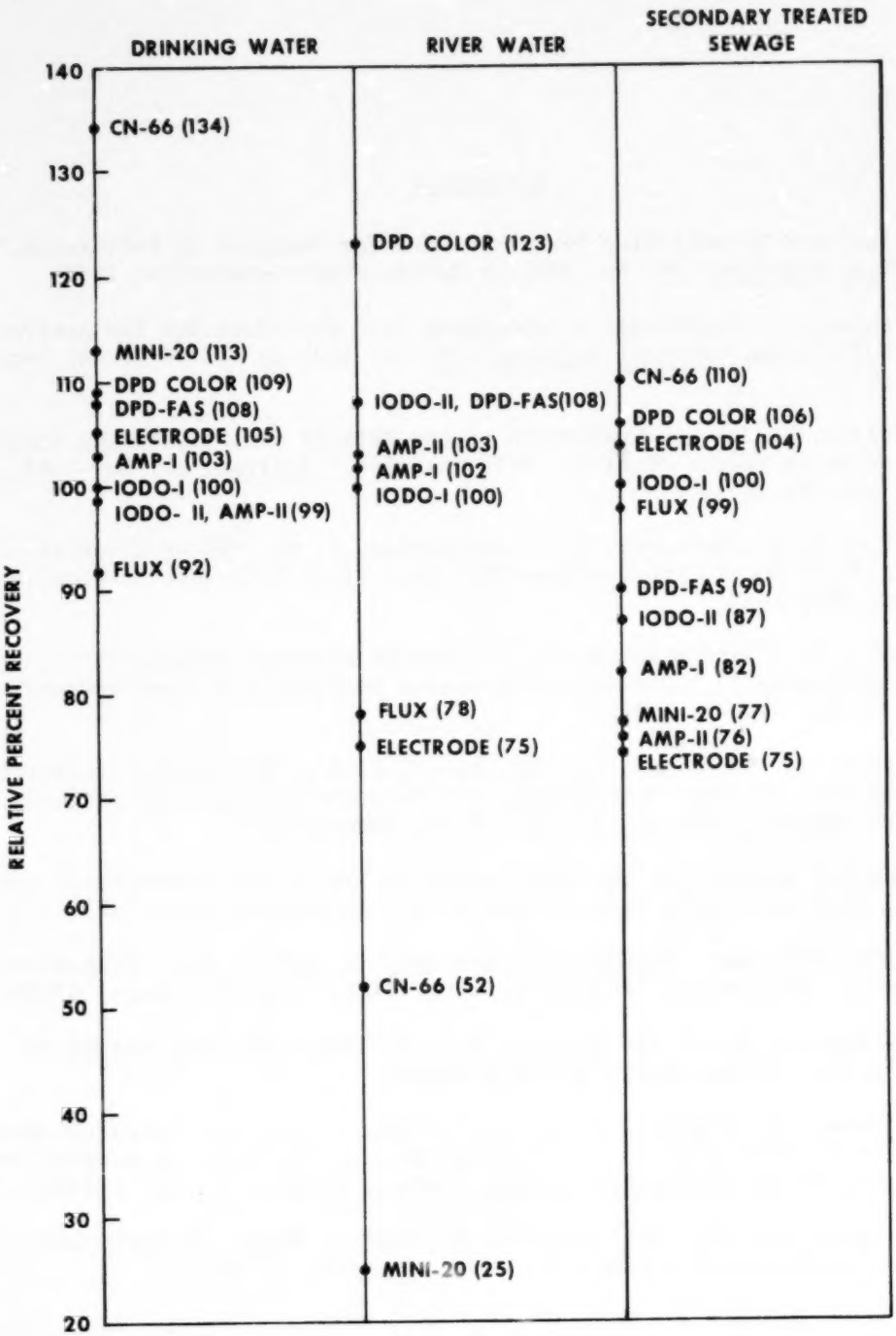

FIGURE 1. ACCURACY RELATIVE TO IODO-I

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